ARKIV FÖR FYSIK Band 2 nr 17

Read 22 February 1950

Evolution of heat during disorder-order transformations in AuCu

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With 4 figures in the text

1. Introduction. The order-disorder transformations in alloys have been studied by measurements of the accompanying variations in structure, volume, resistance, magnetic and elastic properties and internal energy. Though the internal energy is probably the property best fitted for a quantitative control of the theories on this phenomenon, there are few measurements of this kind. For the alloy CuZn Moser (1), and Sykes and Wilkinson (2) have measured the variations of specific heat for increasing temperature from which, in this case, where the discontinuity is of the second order without any discontinuous variation of the energy itself, the internal energy may be determined by integration as a function of the temperature. Sykes and Jones (3) have also tried to apply the same method to the alloy Cu_3Au, where the discontinuity is of the first order though with a rather small discontinuity in the energy. Such measurements, however, leave some uncertainty as to the amount of latent heat. Especially when there is a considerable latent heat, the methods for isothermal measurements of the evolution of heat in quenched specimens, which in this laboratory have been developed and used for the study of precipitation phenomena, could be expected to give better results, and we have now applied such methods to the fifty percent alloy AuCu. For theoretical purposes this alloy was of special interest. Earlier kinetic investigations by X-ray methods carried out by Källbäck, Nyström and Borelius (4) had given a good agreement with a theoretical treatment of the order-disorder transformation in fifty percent alloys given by Borelius (5). The two constants which, according to this theory, determine the internal energy as a function of temperature, had also been determined from the experimental data (6). The internal energy U was thus already pre-calculated some years ago, and a direct determination of U could be expected to give an independent test of the theory.

The problem has been attacked by two independent investigations. The present authors have used an arrangement with specimens in the form of small cylinders, suitable for the study of the relatively slow transformations in the range immediately below the point of discontinuity at 408° C down to about 360° C, whereas Nyström using his method (7) with the specimen in the form of a thin wire, allowing measurements on more rapid transformations, has made calorimetric measurements in the range from 400 down to 335° C combined with resistometric measurements in a wider range. The two investigations are now published at the same time in this journal.

The present investigation has been planned and superintended by Borelius. The laboratory work was started together with Selberg in 1947 and continued with Larsson in 1947–1949. Some preliminary results published by BORELIUS (9) in a survey given at the conference on the physics of metals in Amsterdam in 1948 are surpassed by those published in the present paper.

Our investigations have been supported by grants from the Swedish council for technical research.

2. Experimental arrangements. The principle of the method used is to heat the specimen for some time at a temperature above the critical point and thereupon let it cool down as fast as possible to a temperature below this point and keep it there in a surrounding of very constant temperature. The evolution of heat during the transformation then gives rise to a temperature difference between the specimen and the surroundings, and a series of thermocouples arranged in a suitable way and connected to a sensitive galvanometer give a deflection proportional to this temperature difference, which in turn is proportional to the power of the heat evolved. In order to get the power itself, the arrangement is calibrated by the evolution of a known Peltier effect in a copper-constantan-couple put into a boring in the specimen.

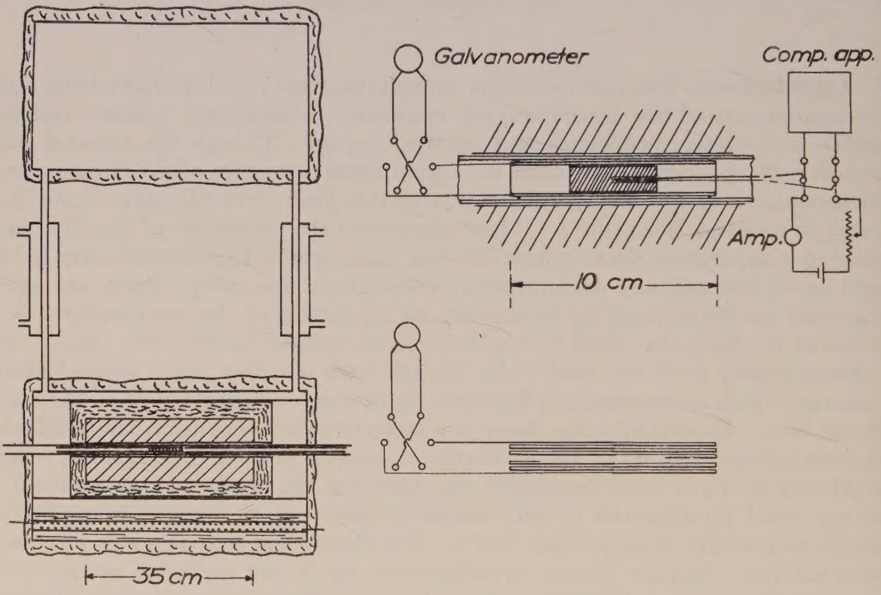

Fig. 1 a. Fig. 1 b.

Fig. 1. Experimental arrangements.

The surrounding of the specimen has to be kept at a very constant temperature. Variations as small as few thousandths of a degree in an hour are disturbing to the measurements. To obtain a constant temperature, the specimen and thermocouples were placed in a boring in a big block of pure aluminium weighing 15 kg, electrically heated by a constant current taken from a voltage regulated motorgenerator.

The temperature outside the bloc was kept constant at about 100° C by a vapour thermostat with water boiling at a constant pressure. The aluminium bloc needed a day at constant current to attain a sufficiently constant temperature. Fig. 1 a gives a general view of the arrangements.

The measuring apparatus, which is in principle very much the same as in earlier investigations in this laboratory, are shown in Fig. 1 b. The specimen is a cylindrical bar of 40 mm length and 12.5 mm diameter, put into a steatite tube with a length of 100 mm, in the wall of which there are 26 channels parallel to the axis. In these channels are threaded 26 welded thermocouples of 0.2 mm Pt and PtRh wires coupled in series and measuring the temperature difference between the centre of the tube, which is influenced by the raised temperature of the specimen, and the ends of the tube, which have a temperature nearer that of the aluminium bloc. The steatite tube is contained in a glass tube filled with nitrogen gas with 5 % hydrogen in order to avoid oxidation of the specimen.

3. The measurements. The specimen was made from pure gold from Ädelmetallbolaget, Malmö, and pure copper from Sieverts Kabelverk, Stockholm. After solidification it was homogenized somewhat below the solidus. The losses in fusion were only 0.003 % and the composition may be given as 50.00 atomic per cent Au.

The preliminary heating of the specimen above the critical point in order to transform it into a disordered state was made by a current through the 26 thermocouples in the wall of the steatite tube. The specimen was generally held for about 20 minutes above the critical point at 408° C, for 6 minutes at the highest temperature 430° C. The temperature was measured by means of the thermocouple in the boring of the specimen. This electric heating raised the temperature of the big aluminium bloc about one degree. After the heating current had been switched off, the thermocouples were connected to the galvanometer over a commutator of copper placed in a Dewar flask to avoid disturbing thermoelectric forces, and the readings on the galvanometer were begun. During the first period of cooling, the specimen lags behind the steatite tube and there is a disturbing deflection of the galvanometer. This fact excludes the investigation of more rapid transformations. Our measurements cover the range from 401° C, where the maximum of the power curve appears after some hours, down to 360° C, where it appears already after 15 minutes. The general shape of the power-time curves (P-t-curves) was everywhere the same.

Fig. 2 gives as an example the curve obtained at 401° C. The time when this specimen passes the critical point on cooling is taken as zero. After the cooling period the power rises to a maximum and then decreases roughly exponentially but not directly to zero. There always appears a buckle on the tail of the curve which shows that the evolution of heat comprises two successive phenomena which, as shown by the dotted curves, may be approximately separated by assuming the first phenomenon to disappear exponentially. To be sure that the real zero point of the power curve (which because of disturbing thermoelectric forces is not exactly the same as zero deflexion of the galvanometer) is reached, one has to continue the measurements over a sufficient period of time. During our earlier series of measurements we were not aware of this complexity and did not always obtain the total heat of transformation.

The calibration of the galvanometer readings into Watts was performed after the power curve had reached zero. It was done by means of the Peltier heat evolved by a current through the couple in the boring of the specimen, the Joule heat being eliminated by commutating the current.

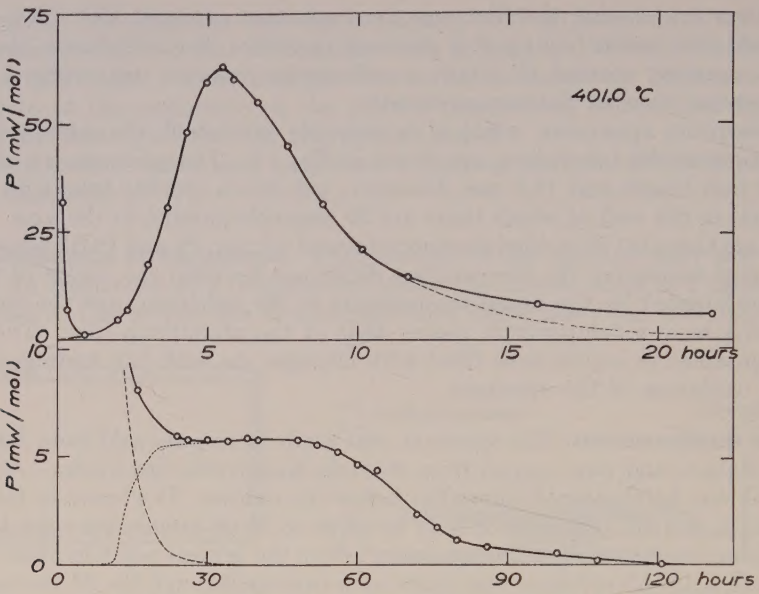

Fig. 2. Experimental power-time curve for 401.0° C.

As we were especially interested in the total heat of transformation, we had to integrate the P–t curves from 0 to ∞. In connection with this integration there are two corrections to be discussed. For small t we have to eliminate the influence of the initial cooling of the specimen. This can be done fairly well by assuming the approach to the P–t curve to be exponential and P itself to be proportional to t^3 for small t (see § 6). The other correction arises because the power P is not exactly proportional to the galvanometer deflexion s. In the second approximation we have

$$P = a s + b \frac{d s}{d t} \tag{1}$$

where a and b are constants. The first part of P is the loss of energy to the surroundings at constant temperature (constant s). The second part is the energy necessary for the rise of the temperature. Though it is well possible to determine b together with a from a discussion of the s—t curves during the calibration with Peltier heat, we have not made such corrections for the second term of Equ. (1), as it has no influence when the P—t curve is integrated from 0 to ∞, s being zero for both limits.

4. Experimental results. Our results are collected in the Tables 1 and 2. Table 1 contains pairs of values of time t and power P from those of our series of measurements which cover the total transformation. The values are chosen in such a way that they allow a good reconstruction of the P—t curves. Table 2 contains values of the heat of transformation obtained by integration of the power curves. The latent heat of the first stage of the transformation (Q_1) was obtainable from all our curves, whereas only six series of measurements where extended enough to allow the determination of the total heat of transformation (Q_{tot}). The heats are given in Joule/mol. One

Table 1

Power P of the evolution of heat in mW/mol t minutes after cooling below the critical point.

360.1 °C		373.2 °C		375.0 °C		385.1 °C		400.0 °C		401.0 °C	
t	P	t	P	t	P	t	P	t	P	t	P
0	3 598	3	2 437	4	2 651	3	1 928	3	364	2	249
2	3 648	5	1 735	7	1 888	5	1 156	8	75.6	10	32.4
4	4 376	7	3 389	9	2 612	7	641	14	16.9	20	6.9
6	3 673	9	3 487	11	2 902	9	568	20	2.5	55	1.2
8	2 725	11	3 253	13	2 618	11	867	50	2.5	120	4.6
12	1 287	13	2 432	17	1 560	13	1 495	80	18.1	140	6.9
16	644	15	1 725	21	880	15	1 928	100	50.6	180	17.3
22	265	19	881	28	271	17	1 871	120	92.5	220	30.6
26	175	25	310	40	70.2	21	1 551	140	140	260	48.0
40	90.3	35	81.6	60	36.8	25	1 017	150	151	300	59.5
60	46.4	65	40.0	90	18.4	33	401	160	155	320	61.8
80	19.5	75	41.2	110	13.4	45	161	170	155	330	63.0
102	10.5	85	40.8	120	10.6	56	51.5	180	149	340	61.8
122	12.0	95	35.1	130	10.0	96	11.0	200	130	350	60.1
146	10.0	105	28.2	150	10.4	116	10.0	240	88.1	400	54.9
165	8.0	120	24.5	170	9.9	136	10.4	280	56.3	460	44.5
185	1.5	500	6.9	190	8.5	186	10.0	310	40.0	530	31.2
205	0.5	800	2.8	210	6.1	286	8.2	370	23.8	610	20.8
250	0.0	1 100	1.6	270	1.4	436	5.8	475	8.1	700	14.5
		1 500	0.0	310	0.2	556	3.7	1 200	5.6	960	8.1
				420	0.0	886	2.5	1 320	5.6	1 580	5.8
						1 500	1.4	1 380	5.6	1 760	5.8
						2 940	0.3	1 440	5.6	2 280	6.1
						3 540	0.0	2 550	3.1	2 880	5.8
								2 670	2.5	3 480	4.9
								2 760	1.9	3 910	3.8
								3 240	0.0	4 280	2.3
										4 800	0.9
										5 710	0.6
										8 070	0.0

mol in this case means 0.5 mol of Cu and Au each, or 130.38 grams of the alloy. Table 2 further contains the logarithms of the half value times $\tau_{1/2}$, that is, the times after which one half of the total heat is evolved. For comparison the last column contains the logarithms of half-value times $\tau'_{1/2}$ for the same temperatures as interpolated from the results of the X-ray investigation of KÄLLBÄCK, NYSTRÖM and BORELIUS (4).

The present calorimetric half-value times agree from 395° C upwards very well with those from the X-ray investigation. The increasing discrepancy at decreasing temperature is no doubt mostly due to the fact that the heat of transformation is evolved so rapidly that the temperature of the specimen at the time when the power-curve reaches its maximum is far above that of the surroundings. The temperatures in the first column of the table thus are not applicable to the half-value times. On the other hand, they are the right ones for the heat of transformation, as the specimen and the surroundings are in thermal equilibrium at the end of the evolution.

5. Discussion of the total heat of transformation. For an alloy with the composition AB BORELIUS (5) found the following set of equations describing the equilibrium states of order-disorder transformations

Table 2

Q_1 heat of transformation in Joule during the first stage, Q_{tot} during the total transformation, $\tau_{\frac{1}{2}}$ half-value time in seconds from this investigation, $\tau'_{\frac{1}{2}}$ from the X-ray investigation of Källbäck, Nyström and Borelius.

°C	Q_1	Q_{tot}	log $\tau_{\frac{1}{2}}$ this inv.	log $\tau'_{\frac{1}{2}}$ K. N. B.
360.1	2 658	2 884	2.56	1.18
373.2	2 503	2 784	2.85	1.86
375.0	2 449	2 646	2.90	1.95
376.6	2 386		2.90	2.04
383.0	2 055		3.10	2.43
384.5	1 905		3.14	2.54
385.1	1 947	2 583	3.16	2.57
389.3	1 775		3.29	2.88
389.8	1 808		3.30	2.95
395.0	1 628		3.48	3.49
399.4	1 319		4.27	4.16
400.0	1 319	2 407	4.28	4.30
401.0	1 339	2 553	4.69	4.56

$$\left.\begin{aligned} &F = U - T S \\ &U = R\left[\alpha q(1-q) + \beta q^2 (1-q)^2\right] \\ &S = R\left[q \ln q + (1-q)\ln(1-q)\right] \\ &\frac{\partial F}{\partial q} = 0 \qquad\qquad 0 < q < \tfrac{1}{2} \end{aligned}\right\} \tag{2}$$

Here F, U and S are the structural parts of free energy, internal energy and entropy per mol, T is the absolute temperature, R the gas constant and q a parameter describing the degree of disorder. These formulae have been successfully applied (6) to the results of an X-ray investigation by KÄLLBÄCK, NYSTRÖM and BORELIUS (4) on the kinetics of the order-disorder transformations in AuCu by choosing for the empirical constants α and β the values $\alpha = 2325$ and $\beta = -2250$. With these values we obtain from (1) the formulae

$$\left.\begin{aligned} &U = R\left[2325\, q(1-q) - 2250\, q^2 (1-q)^2\right] \\ &T = 2325 \frac{1-2q}{\ln \dfrac{1-q}{q}} - 2250 \frac{2q(1-q)(1-2q)}{\ln \dfrac{1-q}{q}} \end{aligned}\right\} \tag{3}$$

from which corresponding values of U and T are obtained by inserting different values of q from 0 to 0.5. We thus obtain with $R = 8{,}314$ Joule/mol. degree the set of values for q, $t = T - 273.16$, U, and the heat of transformation $Q = U_{q=0.5} - U$, given in Table 3. Q is the quantity to be compared with our experimental values.

In figure 3 the curves show the calculated values of U increasing upwards, and of Q increasing downwards in their dependence on the temperature. The circles show the experimental values for the final state of equilibrium and the crosses for the intermediate state reached after the first stage of transformation. The experimental

Table 3

Precalculated values of the internal energy U and heat of transformation Q in Joule/mol.

q	°C	U	Q
0	− 273.2	0	3 663
0.04	349.9	714	2 949
0.045	361.8	796	2 867
0.05	372.2	876	2 787
0.06	389.2	1 030	2 633
0.07	402.5	1 179	2 484
0.5	> 408	3 663	0

results concerning the total heat of transformation agree within the limits of experimental uncertainty, exactly with the pre-calculated values.

It is remarkable that there seems to be no appreciable jump in the energy temperature-curve at about 380° C in spite of the fact found by JOHANSSON and LINDE (9), and now further stated by NYSTRÖM (10), that the equilibrium structures are different at both sides of this temperature. The two structures Cu Au I, stable below 380, and Cu Au II, stable above this temperature, thus seem to differ very little as regards the internal energy.

6. Conclusions concerning nucleation and growth of ordered domains. Our measurements are all within the range of temperature where, according to the theory, there is a thermodynamic potential barrier between the unstable disordered and the

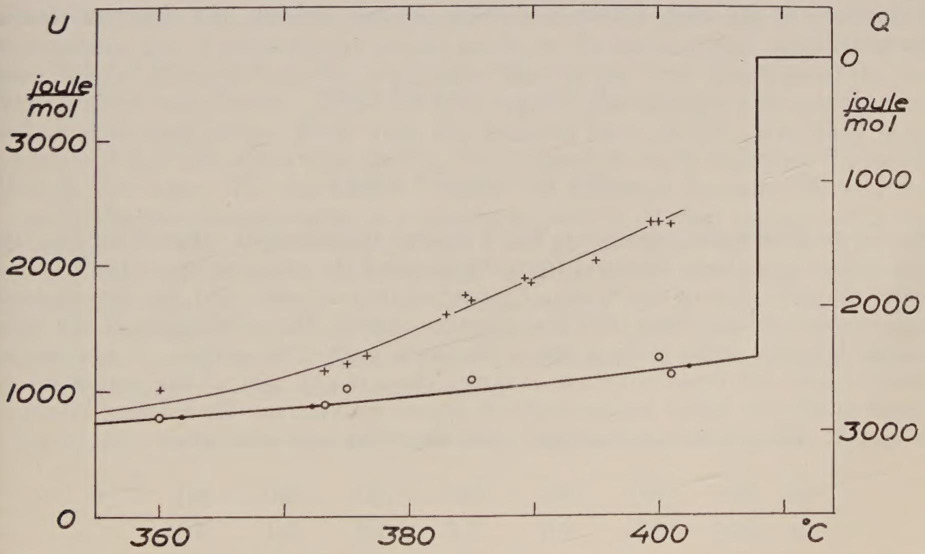

Fig. 3. Internal energy U and heat of transformation Q as a function of temperature. Filled points precalculated values, and circles experimental values for the equilibrium states. Crosses experimental values for the intermediate states.

stable ordered states. For this case the scheme of crystallisation outlined by TAMMANN is most probable, with velocity of nucleation and velocity of crystal growth as the main factors determining the kinetics of a structural transformation. Adopting this scheme we may perform an approximate calculation of the heat effect as a function of time at the beginning of the transformation, when the ordered domains are still small and far apart from each other. We denote the time from the moment of quenching as t and assume that for small t the number of nuclei of the ordered state in a unit of volume is approximately $N = nt$, where n, the number of nuclei formed in unit of time, is constant. The number of nuclei appearing in the interval between $t = \Theta$ and $\Theta + d\Theta$ then is

$$dN = n\,d\Theta \tag{4}$$

If these nuclei grow in one, two or three dimensions with constant velocity, they will at a time $t > \Theta$ have a total volume

$$dV = dN \cdot b \cdot (t - \Theta)^x = nb\,(t - \Theta)^x\,d\Theta \tag{5}$$

where x is 1, 2 or 3 in the different cases. The value of the constant b is dependent on the geometry of the crystal growth. (If, for instance, the growth is spherical, b is $4\pi v^3/3$, where v is the linear velocity of crystallisation.) The total volume of all ordered domains grown in the time from 0 to t is

$$V = \int_0^t nb\,(t - \Theta)^x\,d\Theta = nb\frac{t^{x+1}}{x+1}. \tag{6}$$

If further c is the heat of transformation per unit volume, the observed thermal power is

$$P = c\frac{dV}{dt} = cnb\,t^x = a\,t^x \tag{7}$$

or

$$\log P = \log a + x \log t \tag{8}$$

In order to determine x we have in Fig. 4 plotted experimental values of $\log P$ against $\log t$, where t has been reckoned from the moment the temperature of the specimen passes the critical point on cooling. If equation (8) had been valid, the curves should have risen as straight lines from low negative values. The overlapping of the initial cooling, however, hides more or less of the initial part of the curves. At low temperatures, where the transformation is rapid, the straight part of the curves do not appear at all. At higher temperatures it appear well enough for a determination of the slopes. The slopes from the figure give the following values of x

at	385	390	397	399	400	400	401	° C
x	(2.9)	(3.5)	3.0	3.4	3.8	3.1	3.1	

Within the limits of error x is equal to 3 and it seems most probable that the ordered domains, as could be expected, grow in three dimensions.

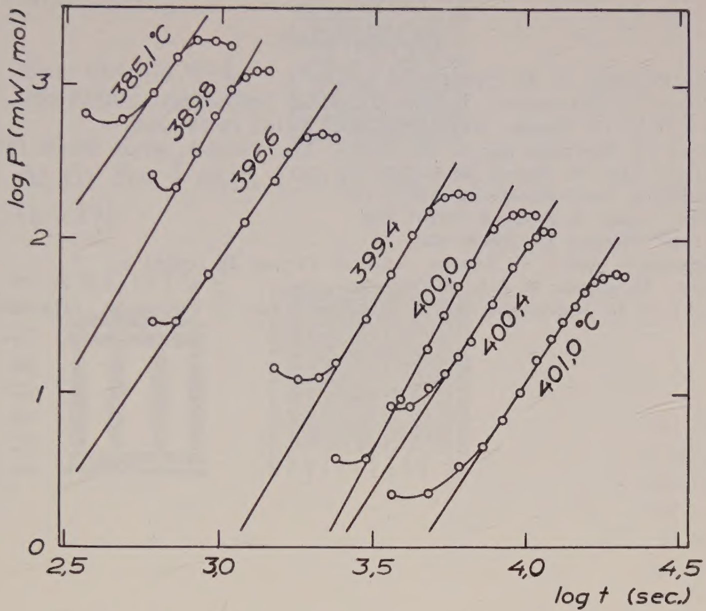

Fig. 4. Logarithm of power against logarithm of time.

7. The intermediate states. The intermediate states, the existance of which is clearly demonstrated by our calorimetric results, are most probably connected with certain complications which were discussed already in 1928 by Borelius, Johansson and Linde (11). The disorder-order transition in CuAu gives rise to a tetragonal deformation, and if there appear several nuclei in the same crystal grain, they will cause ordered domains with their axes distributed in the three directions of the axes of the original cubic lattice. These domains cannot unite directly when growing into contact with each other. Even when the domains have parallel axes, they might not unite if they are out of step, that is if a Cu-plane in one is continued by an Au-plane in the other. The boundaries between the different domains will represent a zone of disorder corresponding to a certain amount of internal energy, which cannot disappear without the rearrangement of all atoms within whole domains, and thus probably will disappear rather slowly. Another source of internal energy that will probably disappear slowly, is the potential energy due to stresses occurring between the ordered domains with different directions of their axes. For the present, however, we cannot decide which of these contributions is the dominating part of the residual energy of the intermediate states.

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LITERATURE

1. H. Moser. Physikal. Z. **37** (1936) 737.
2. C. Sykes and H. Wilkinson. J. inst. Metals **61** (1937) 223.
3. C. Sykes and F. W. Jones. Proc. Roy. Soc. A 157 (1936) 213.
4. O. Källbäck, J. Nyström and G. Borelius. Ing. Vetensk. Akad. Hand. **157** (1941).
5. G. Borelius. Ann. d. Physik **20** (1934) 57.
6. G. Borelius. J. Inst. Metals **74** (1947) 17.
7. J. Nyström. Arkiv f. Fysik **1** (1949) 359.
8. G. Borelius. Physica **15** (1949) 935.
9. C. H. Johansson and J. O. Linde. Ann. d. Physik **25** (1936) 1.
10. J. Nyström. To appear in Ark. f. Fysik.
11. G. Borelius, C. H. Johansson and J. O. Linde. Ann. d. Physik **86** (1928) 291.

Tryckt den 29 april 1950.

Uppsala 1950. Almqvist & Wiksells Boktryckeri AB